

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-004083

(43)Date of publication of application : 06.01.1998

(51)Int.Cl.

H01L 21/3065

C01B 21/06

H01L 21/205

H01L 21/68

// C23C 16/44

(21)Application number : 08-155798 (71)Applicant : KYOCERA CORP

(22)Date of filing : 17.06.1996 (72)Inventor : ITOU YUMIKO
AIDA HIROSHI

(54) ANTICORROSIVE MATERIAL FOR SEMICONDUCTOR FABRICATION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an anticorrosive material having a higher corrosion resistance than SiO₂, Al₂O₃, AlN, etc.

SOLUTION: A part of a product to be exposed to a fluoric corrosive gas such as SF₆, CF₄, CHF₃, ClF₃ and HF or its plasma is made from a compd. thin film or single crystal. The product is e.g. a Si wafer clamp ring, upper electrode shield ring, or inner wall of a plasma treating apparatus, etching apparatus, etc., for the semiconductor fabrication. The compd. is an oxide, nitride, carbide or fluoride of 3a elements on the periodic table, e.g. Sc, La, Ce, Eu and Dy.

CLAIMS

[Claim(s)]

[Claim 1] the part put to fluorine system corrosion gas or its plasma -- the [periodic table] -- the corrosion-resistant member for semi-conductor manufacture characterized by consisting of a 3a group element compound.

[Claim 2] the [said / periodic table] -- the corrosion-resistant member for semi-conductor manufacture according to claim 1 characterized by being at least one sort as which 3a group element was chosen from the group of Sc, La, Ce, Eu, and Dy.

[Claim 3] The corrosion-resistant member for semi-conductor manufacture according to claim 1 characterized by said compound consisting of an oxide, a nitride, carbide, fluorides, and those complex.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the corrosion-resistant member suitable for fixtures, such as wall material in the plasma treatment equipment used for manufacturing the semiconductor device as which high corrosion resistance is required from fluorine system corrosive gas or its plasma, and membrane formation equipment, and supporter material which supports Si substrate.

[0002]

[Description of the Prior Art] Use of plasma, such as a dry process, plasma jet flame coating, etc. of semi-conductor manufacture, is progressing quickly in recent years. For example, in the semi-conductor manufacture process, the halogen system corrosion gas of a fluorine system is especially used abundantly from the reactant height as deposition, the object for etching, or an object for cleaning in the plasma process.

[0003] Moreover, in order to prevent the corrosion by gas or the plasma in the part in contact with the above-mentioned gas and the plasma in equipment, such as a wall, they are SiO(s)2, such as glass from the former, and a quartz. Corrosion-resistant metals, such as an ingredient used as a principal component, and stainless steel, Monel, are used.

[0004] Furthermore, in semiconductor fabrication machines and equipment, in order that the susceptor material holding Si wafer etc. may also contact corrosive gas and the plasma, what carried out CVD coating of the alumina sintered compact which was excellent in corrosion resistance conventionally, sapphire and the sintered compact of AlN, or these on the base front face is used. Moreover, the heater which coated graphite and boron nitride also as a heater in equipment is used.

[0005]

[Problem(s) to be Solved by the Invention] however, if glass and the quartz of the corrosion resistance in the plasma which are used conventionally are inadequate, and consumption is intense and touches a fluorine, the contact surface will etch -- having - a front face -- description changed, and the front face was blooming cloudy with the member for which light transmission nature is needed white gradually, and the problem of translucency falling had arisen.

[0006] Moreover, since the corrosion resistance of the member which used metals, such as stainless steel, is inadequate, a corrosion rate causes defective generating quickly mixed into a manufacture as an impurity again. Moreover, if the alumina and AlN sintered compact with which use is progressing also touch the plasma at an elevated temperature noting that it excels in corrosion resistance to fluorine system gas, corrosion will advance, degraining of the crystal grain child from the front face of a sintered compact will arise, and it will become the cause of contamination too.

[0007]

[Means for Solving the Problem] Then, the thing for which a fluoride will be generated by the front face if a reaction with fluorine system corrosion gas or its plasma advances as a result of this invention persons' examining the ingredient which has the corrosion resistance which was excellent to fluorine system corrosion gas or its plasma, and as that the stability of the fluoride has affected corrosion resistance greatly, and a fluoride the [periodic table] -- as a corrosion resistance member since the fluoride of 3a group element has the high melting point and it is stable in an elevated temperature -- the [periodic table] -- it resulted that 3a group element compound was suitable in header this invention.

[0008] namely, the part which the corrosion-resistant member for semi-conductor manufacture of this invention is completed based on the above-mentioned knowledge, and contacts fluorine system corrosion gas or its plasma -- the [periodic table] -- it is characterized by constituting with 3a group element compound.

[0009] especially -- the [said / periodic table] -- 3a group element is further characterized by to be at least one sort chosen from the group of Sc, Y, La, Ce, Yb, Eu, and Dy, and said compound consisting of an oxide, a nitride, carbide, fluorides, and those complex.

[0010] By the part put to fluorine gas or its plasma, the front face becomes a fluoride, and evaporates and consumption progresses. the member which is put to fluorine system gas or its plasma according to this invention -- the [periodic table] -- constituting with 3a group element compound -- the [periodic table] -- 3a group element generates a fluoride layer with the high melting point by the reaction with a fluorine, and improvement in the endurance in a severe fluorine system gas ambient atmosphere is attained in a broad temperature requirement.

[0011]

[Embodiment of the Invention] The corrosion-resistant member of this invention is a member put to the plasma containing fluorine system gas or fluorine system gas, and as fluorine system gas, it is gas, such as SF₆, CF₄, CHF₃, ClF₃, and HF, and if microwave, a RF, etc. are introduced into the ambient atmosphere into which these gas was introduced, these gas will be plasma-ized.

[0012] the part which is put to such fluorine system gas or its plasma according to this invention -- the [periodic table] -- it constitutes from a 3a group element compound. here -- the [periodic table] -- as a 3a group element, it is Y, Sc, and a lanthanoids system element, and at least one sort chosen from the group of Sc, La, Ce, Eu, and Dy also in them has the most desirable melting point as a fluoride from a high thing as compared with elements other than these.

[0013] the [moreover, / periodic table] -- as 3a group element compound -- Sc₂O₃, Y₂O₃, Yb₂O₃, Er₂O₃, and Dy₂O₃ etc. -- carbide, such as nitrides, such as an oxide, and ScN, YN, and YC, YF₃, and LaF₃ etc. -- a fluoride etc. is mentioned. If each of these compounds is exposed to fluorine system corrosive gas or the plasma, all will change to a fluoride.

[0014] this corrosion-resistant member -- a predetermined base front face -- the [said / periodic table] -- it is desirable to cover with the thin film forming method of common knowledge of 3a group element compound in respect of compactness. In that case, especially on the surface of a base, it is good to form by 10-200 micrometers the thickness of 5-500 micrometers. For a corrosion resistance thin film to disappear and it is for a base to be exposed, when thickness was too thin and corrosion advances by corrosive gas. Such precise film may be a thin film formed by gaseous-phase methods, such as a thin film which applied the liquid phase with the well-known sol gel process, and was calcinated, a well-known CVD method, and PVD.

[0015] the [in addition, / periodic table] -- it is also possible the single crystal which consists of a 3a group element compound, and to constitute from a precise sintered compact. In this case, as for each of especially these bulk objects, it is desirable for relative density to be 99% or more 98% or more. This is for corrosion resistance to fall, so that many voids exist. such a sintered compact -- the [periodic table] -- although it can create by calcinating this Plastic solid after fabricating in a predetermined configuration using the powder of 3a group element compound -- general -- the [periodic table] -- 3a group element compound can attain densification by calcinating impressing a high pressure gas ambient atmosphere by the hydrostatic-

pressure calcinating method between heat etc., since it is a difficulty degree of sintering.

[0016]

[Example] as various glass as shown in Table 1, a sintered compact, a single crystal, and a base -- carbon -- using -- PVD -- the [periodic table] -- the thin film with a thickness of 20 micrometers it is thin from 3a group oxide, a nitride, carbide, and a fluoride was formed. These are installed in a RIE plasma etching system, and it is CF₄. O₂ Mixed gas (CF₄:O₂ =9:1), and Ar and SF₆ While introducing either of mixed gas (Ar:SF₆ = 2:3), the 13.56MHz RF was introduced and the plasma was generated. It held in this plasma for a maximum of 3 hours, weight reduction of the ingredient before and behind processing was measured, and the thickness (etching rate) into which per minute is etched was computed from that value. Moreover, the front face after a trial was observed and the result was shown in Table 1.

[0017]

[Table 1]

[0018] SiO₂ used from the former so that clearly from the result of Table 1 In glass and a nitriding cay genius sintered compact An etching rate is aluminum 2O₃ known as an ingredient which exceeds 500A / min and was excellent in corrosion resistance. A sintered compact, an AlN sintered compact, and AlF₃ Although below 150A / min, and an etching rate become small then the [based on this invention / periodic-table] - with 3a group element compound, it turns out that corrosion resistance of an etching rate improves by leaps and bounds below 20A / min. Also in these, especially each Sc, La, Ce, Eu, and Dy compound showed the further excellent property below 10A / min.

[0019]

[Effect of the Invention] The corrosion-resistant member for semi-conductor manufacture of this invention has corrosion resistance high as a member put to fluorine system corrosive gas and its plasma, and can attain reinforcement of these members by using it for the shield ring of the circumference of the clamp ring and up electrode for Si wafer immobilization in plasma treatment equipment and the etching system which are specifically used as an object for semi-conductor manufacture, equipment wall material, etc. as explained in full detail above.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the corrosion-resistant member suitable for fixtures, such as wall material in the plasma treatment equipment used for manufacturing the semiconductor device as which high corrosion resistance is required from fluorine system corrosive gas or its plasma, and membrane formation equipment, and supporter material which supports Si substrate.

PRIOR ART

[Description of the Prior Art] Use of plasma, such as a dry process, plasma jet flame coating, etc. of semi-conductor manufacture, is progressing quickly in recent years. For example, in the semi-conductor manufacture process, the halogen system corrosion gas of a fluorine system is especially used abundantly from the reactant

height as deposition, the object for etching, or an object for cleaning in the plasma process.

[0003] Moreover, in order to prevent the corrosion by gas or the plasma in the part in contact with the above-mentioned gas and the plasma in equipment, such as a wall, they are SiO_2 , such as glass from the former, and a quartz. Corrosion-resistant metals, such as an ingredient used as a principal component, and stainless steel, Monel, are used.

[0004] Furthermore, in semiconductor fabrication machines and equipment, in order that the susceptor material holding Si wafer etc. may also contact corrosive gas and the plasma, what carried out CVD coating of the alumina sintered compact which was excellent in corrosion resistance conventionally, sapphire and the sintered compact of AlN, or these on the base front face is used. Moreover, the heater which coated graphite and boron nitride also as a heater in equipment is used.

EFFECT OF THE INVENTION

[Effect of the Invention] The corrosion-resistant member for semi-conductor manufacture of this invention has corrosion resistance high as a member put to fluorine system corrosive gas and its plasma, and can attain reinforcement of these members by using it for the shield ring of the circumference of the clamp ring and up electrode for Si wafer immobilization in plasma treatment equipment and the etching system which are specifically used as an object for semi-conductor manufacture, equipment wall material, etc. as explained in full detail above.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] however, if glass and the quartz of the corrosion resistance in the plasma which are used conventionally are inadequate, and consumption is intense and touches a fluorine, the contact surface will etch -- having - a front face -- description changed, and the front face was blooming cloudy with the member for which light transmission nature is needed white gradually, and the problem of translucency falling had arisen.

[0006] Moreover, since the corrosion resistance of the member which used metals, such as stainless steel, is inadequate, a corrosion rate causes defective generating quickly mixed into a manufacture as an impurity again. Moreover, if the alumina and AlN sintered compact with which use is progressing also touch the plasma at an elevated temperature noting that it excels in corrosion resistance to fluorine system gas, corrosion will advance, degraining of the crystal grain child from the front face of a sintered compact will arise, and it will become the cause of contamination too.

MEANS

[Means for Solving the Problem] Then, the thing for which a fluoride will be generated by the front face if a reaction with fluorine system corrosion gas or its plasma advances as a result of this invention persons' examining the ingredient which has the corrosion resistance which was excellent to fluorine system corrosion gas or its plasma, and as that the stability of the fluoride has affected corrosion resistance

greatly, and a fluoride the [periodic table] -- as a corrosion resistance member since the fluoride of 3a group element has the high melting point and it is stable in an elevated temperature -- the [periodic table] -- it resulted that 3a group element compound was suitable in header this invention.

[0008] namely, the part which the corrosion-resistant member for semi-conductor manufacture of this invention is completed based on the above-mentioned knowledge, and contacts fluorine system corrosion gas or its plasma -- the [periodic table] -- it is characterized by constituting with 3a group element compound.

[0009] especially -- the [said / periodic table] -- 3a group element is further characterized by to be at least one sort chosen from the group of Sc, Y, La, Ce, Yb, Eu, and Dy, and said compound consisting of an oxide, a nitride, carbide, fluorides, and those complex.

[0010] By the part put to fluorine gas or its plasma, the front face becomes a fluoride, and evaporates and consumption progresses. the member which is put to fluorine system gas or its plasma according to this invention -- the [periodic table] -- constituting with 3a group element compound -- the [periodic table] -- 3a group element generates a fluoride layer with the high melting point by the reaction with a fluorine, and improvement in the endurance in a severe fluorine system gas ambient atmosphere is attained in a broad temperature requirement.

[0011]

[Embodiment of the Invention] The corrosion-resistant member of this invention is a member put to the plasma containing fluorine system gas or fluorine system gas, and as fluorine system gas, it is gas, such as SF₆, CF₄, CHF₃, ClF₃, and HF, and if microwave, a RF, etc. are introduced into the ambient atmosphere into which these gas was introduced, these gas will be plasma-ized.

[0012] the part which is put to such fluorine system gas or its plasma according to this invention -- the [periodic table] -- it constitutes from a 3a group element compound. here -- the [periodic table] -- as a 3a group element, it is Y, Sc, and a lanthanoids system element, and at least one sort chosen from the group of Sc, La, Ce, Eu, and Dy also in them has the most desirable melting point as a fluoride from a high thing as compared with elements other than these.

[0013] the [moreover, / periodic table] -- as 3a group element compound -- Sc₂O₃, Y₂O₃, Yb₂O₃, Er₂O₃, and Dy₂O₃ etc. -- carbide, such as nitrides, such as an oxide, and ScN, YN, and YC, YF₃, and LaF₃ etc. -- a fluoride etc. is mentioned. If each of these compounds is exposed to fluorine system corrosive gas or the plasma, all will change to a fluoride.

[0014] this corrosion-resistant member -- a predetermined base front face -- the [said / periodic table] -- it is desirable to cover with the thin film forming method of common knowledge of 3a group element compound in respect of compactness. In that case, especially on the surface of a base, it is good to form by 10-200 micrometers the thickness of 5-500 micrometers. For a corrosion resistance thin film to disappear and it is for a base to be exposed, when thickness was too thin and corrosion advances by corrosive gas. Such precise film may be a thin film formed by gaseous-phase methods, such as a thin film which applied the liquid phase with the well-known sol gel process, and was calcinated, a well-known CVD method, and PVD.

[0015] the [in addition, / periodic table] -- it is also possible the single crystal which consists of a 3a group element compound, and to constitute from a precise sintered compact. In this case, as for each of especially these bulk objects, it is desirable for relative density to be 99% or more 98% or more. This is for corrosion resistance to fall, so that many voids exist. such a sintered compact -- the [periodic table] --

although it can create by calcinating this Plastic solid after fabricating in a predetermined configuration using the powder of 3a group element compound -- general -- the [periodic table] -- 3a group element compound can attain densification by calcinating impressing a high pressure gas ambient atmosphere by the hydrostatic-pressure calcinating method between heat etc., since it is a difficulty degree of sintering.

EXAMPLE

[Example] as various glass as shown in Table 1, a sintered compact, a single crystal, and a base -- carbon -- using -- PVD -- the [periodic table] -- the thin film with a thickness of 20 micrometers it is thin from 3a group oxide, a nitride, carbide, and a fluoride was formed. These are installed in a RIE plasma etching system, and it is CF₄. O₂ Mixed gas (CF₄:O₂ =9:1), and Ar and SF₆ While introducing either of mixed gas (Ar:SF₆ = 2:3), the 13.56MHz RF was introduced and the plasma was generated. It held in this plasma for a maximum of 3 hours, weight reduction of the ingredient before and behind processing was measured, and the thickness (etching rate) into which per minute is etched was computed from that value. Moreover, the front face after a trial was observed and the result was shown in Table 1.

[0017]

[Table 1]

[0018] SiO₂ used from the former so that clearly from the result of Table 1 In glass and a nitriding cay genius sintered compact An etching rate is aluminum 2O₃ known as an ingredient which exceeds 500A / min and was excellent in corrosion resistance. A sintered compact, an AlN sintered compact, and AlF₃ Although below 150A / min, and an etching rate become small then the [based on this invention / periodic-table] - with 3a group element compound, it turns out that corrosion resistance of an etching rate improves by leaps and bounds below 20A / min. Also in these, especially each Sc, La, Ce, Eu, and Dy compound showed the further excellent property below 10A / min.